Cu_2O Shape Transition During Cu-Au Oxidation

G.-W Zhou[a], J. A. Eastman[a], R. C. Birtcher[a], P. M. Baldo[a], J. E. Pearson[a], L. Wang[b], J. C. Yang[b]
[a] Materials Science Division, Argonne National Laboratory
[b] Department of Materials Science and Engineering, University of Pittsburgh

Motivation

A general strategy for the protection of underlying metals is alloying, which leads to the formation of a protective oxide layer over the alloy surface due to the preferential oxidation of one component of the alloy, two key factors control protective oxide layer formation during alloy oxidation:

- Oxide thermodynamic stability
- Oxide structural continuity

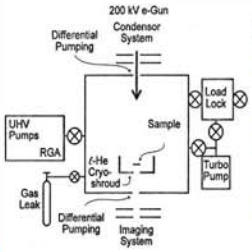
Our study of (001)Cu-Au oxidation

Understand the effect of oxide island morphology on the formation of continuous oxide film during alloy oxidation

Accomplishments and impacts

- Cu_2O islands on Cu-Au undergo a dendritic transition from initially compact shape as growth proceeds
- Demonstrate a non-uniform surface composition develops during Cu-Au oxidation
- Dendritic morphology of oxide islands prevent formation of protective, continuous oxide overlay on metal alloys
- A new approach to creating complex oxide patterns on metal surfaces.

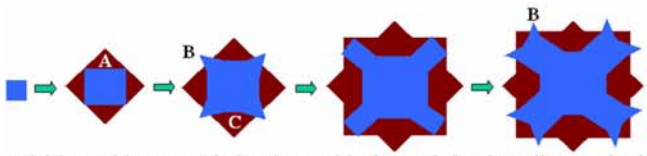
Experimental approach



In-situ environmental transmission electron microscope (MRL, UIUC)

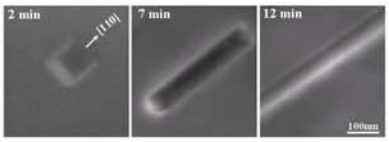
- Visualization of oxidation in real time
- Nanometer scale information
- Information on buried interface
- Local reaction rate and the size and structural evolution of single oxide islands

Proposed mechanism



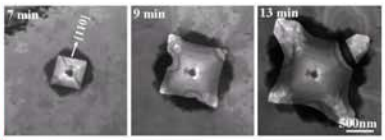
Dendritic oxide growth in the oxidation of Cu-Au alloys, *A:* Au-rich zone, *B*: growth controlled by oxygen surface diffusion, *C:* growth limited by diffusion through a Au-rich zone.

Comparison (001)Cu and (001)Cu-Au oxidation



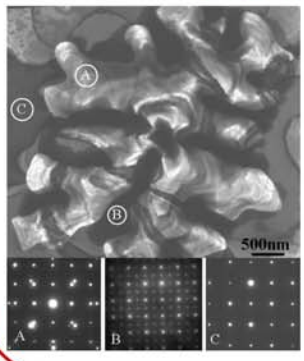
at 600°C in 5×10^{-4} Torr

Square-elongation transition of Cu_2O islands during (001)Cu oxidation



Dendrtic transition of the initially square-shaped Cu_2O islands during (001)Cu-5at.%Au oxidation

Composition evolution



Typical morphology of dendritic oxide obtained during oxidation of (001)Cu-15at.%Au films at 600°C in $pO_2= 5\times10^{-4}$ Torr.

A) epitaxial Cu_2O islands

B) $CuAu_3$ ordered phase has formed

C) Cu-15at.%Au

Future directions and speculation

Dendritic growth: general behavior?

- Alloy systems containing noble metals (Au, Pt, Ag) and oxidizable metals (Cu, Fe, Ni, etc)
- Alloy systems containing two oxidizable metals, but one is more noble than the other

Predictable and controllable?

- Theoretical understanding of the relative importance of diffusivities of reactive species on the oxide growth
- Atomic-scale simulation of dendritic oxide growth

G.-W Zhou, L. Wang, R. C. Birtcher, P. M. Baldo, J. E. Pearson, J. C. Yang, J. A. Eastman, "Cu_2O shape transition during Cu-Au oxidation" (submitted for publication)

ARGONNE NATIONAL LABORATORY

This work was supported by the U.S. Department of Energy, Basic Energy Sciences, under contract W-31-109-ENG-38.

THE UNIVERSITY OF CHICAGO

Office of Science U.S. DEPARTMENT OF ENERGY